Hydrogen Bond Studies

69.* A Proton Magnetic Resonance Study of Solid Monomethylammonium Chloride

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Proton magnetic resonance line shape and second moment data are reported for the β and γ forms of CH_3NH_3Cl, CD_3NH_3Cl, and CH_3ND_3Cl. The two forms show distinctly different behaviour, consistent with previous NMR spin-lattice relaxation time measurements.

The present paper is the fourth in a series dealing with the NMR spectra of solid methyl substituted ammonium salts. The previous papers include a spin-lattice relaxation study of monomethylammonium chloride [1] and second moment studies of di- and trimethylammonium chloride.[2,3]

Solid monomethylammonium chloride is known to exist in three different forms α ($T > 264$ K), γ ($220 < T < 264$ K) and β ($T < 220$ K).[4-7] The γ form may be supercooled into the stability range of the β phase down to liquid nitrogen temperature without transforming to the β form. From the relaxation time data it is clear that the reorientation behaviour of the methylammonium ion is different in the three polymorphs. This difference was not apparent from line-width data reported recently by Tsau and Gilson.[8] Furthermore, it is not immediately clear from their paper which of the three forms their data refer to. It will be shown in the present paper that the temperature dependence of the line widths and line shapes of the β and γ phases differ considerably, in agreement with the relaxation data.

EXPERIMENTAL

The samples used in the present NMR line-width study were obtained from the same source as those used in the T_1 measurements,[1] and were purified in the same way.

Proton spectra were recorded at 16 MHz with the normal precautions taken to avoid saturation and excessive modulation broadening. Much of the detail concerning the re-

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cording of spectra and the evaluation of experimental second moments is described in a previous paper.[9] For some of the spectra a time-averaging computer (Varian Assoc. C-1024) was used in order to improve the signal-to-noise ratio.

Special care was taken to ensure that the desired phase was obtained at a given temperature. In particular, the γ form was in most cases obtained by heating the β form rather than by cooling the α form, since the $\alpha \rightarrow \gamma$ transition occurred in a somewhat unpredictable way depending on the cooling rate. Furthermore, due to the drastic T_1 changes at the transitions, the saturation behaviour could be used to test the progress of these transitions.

Within the range of any particular phase, the measurements were made both for increasing and decreasing temperatures between consecutive spectra without any noticeable hysteresis effect on the second moments or line shapes.

RESULTS AND DISCUSSION

Data are given only for the β and γ phases since the α phase was covered adequately by Tsau and Gilson.[8] Their results show that the α phase spectra are completely narrowed throughout the stability range by rapid reorientation of the $CH_3NH_3^+$ ion about the $C-N$ axis. The experimental second moments for the β and γ phases of CH_3NH_3Cl, CD_3NH_3Cl, and CH_3ND_3Cl are shown in Figs. $1-3$ and the line shapes of β and γ CH_3NH_3Cl at 133 K are shown in Fig. 4.
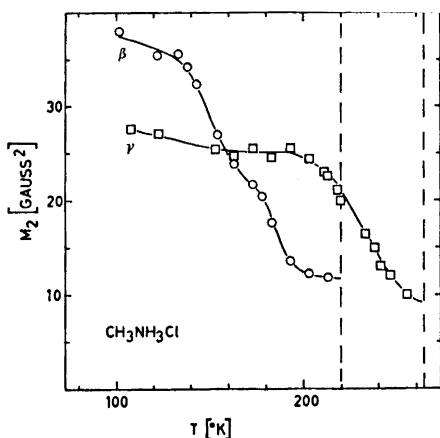

Fig. 1. The temperature dependence of the proton magnetic resonance second moment for CH_3NH_3Cl. The vertical dashed lines indicate (from the left) the temperature of the phase transitions β to γ and γ to α. The measured second moments are denoted for the γ phase by squares and for the β phase by circles.
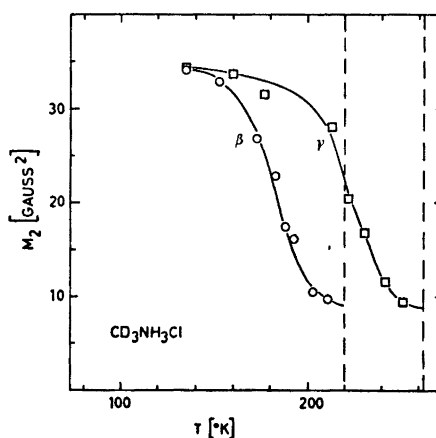
Fig. 2. The temperature dependence of the proton magnetic resonance second moment for CD_3NH_3Cl. Notation is the same as in Fig. 1.

1. γ *Phase.* The T_1 relaxation data showed a distinct difference between the CH_3 and NH_3 group in terms of reorientation barriers and frequencies. This feature is apparent also from the present line width and line shape data.
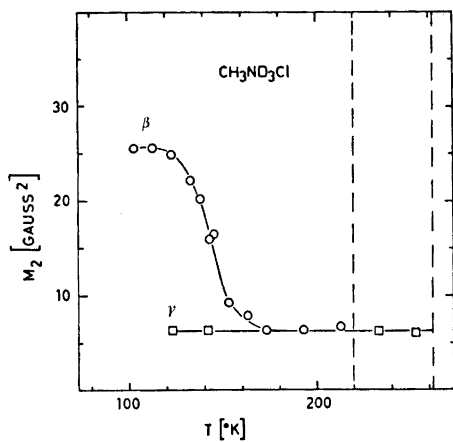
Fig. 3. The temperature dependence of the proton magnetic resonance second moment for CH_3ND_3Cl. Notation is the same as in Fig. 1.
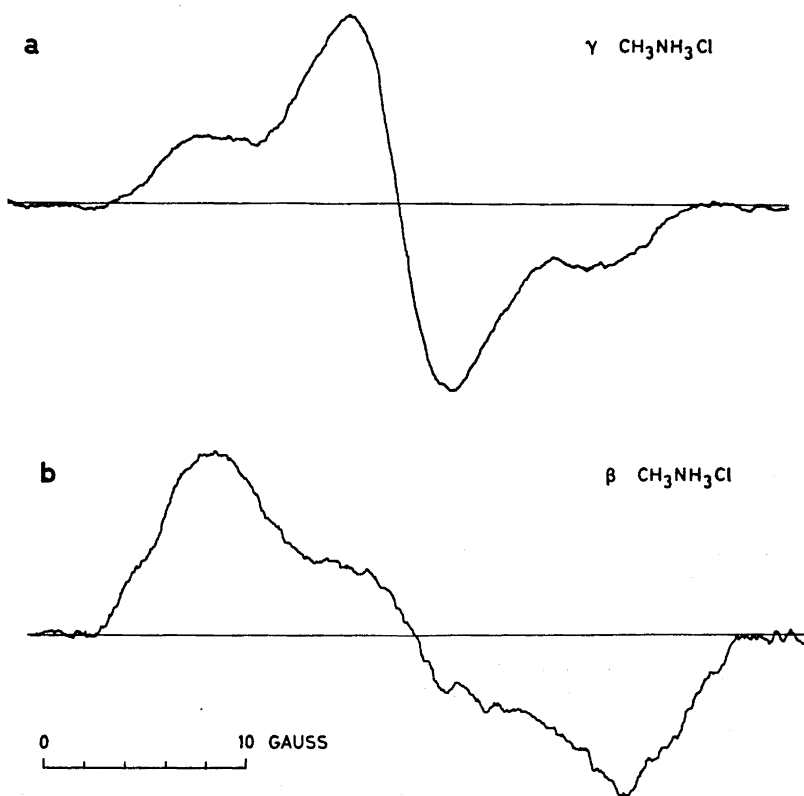

Fig. 4. The shape of the proton resonance at 133 K for β CH_3NH_3Cl and for supercooled γ CH_3NH_3Cl.

The CH_3ND_3Cl spectrum has the shape of that of a rotating CH_3 group down to 100 K and the second moment is approximately constant (6.2 G^2) down to this temperature. This value is close to the value 6.3 G^2 calculated for a rotating CH_3 group in CH_3ND_3Cl by Tsau and Gilson.[8] Clearly no reorientation barrier for the CH_3 group can be obtained from the present line-width data for the γ phase, since no line-width transition is observed. It may at least be shown, however, that the activation energy of 2.5 kcal/mol obtained from the T_1 data is consistent with the lack of broadening down to 100 K. Stejskal and Gutowsky [10] have computed the average tunneling frequency as a function of temperature for a methyl group in a 3-fold cosine potential with various barrier heights. Application of their data to a barrier of 2.8 kcal/mol (allowing 0.3 kcal/mol for zero-point vibrational energy), a tunneling frequency of at least 10^7 Hz is found at 100 K. This is certainly rapid enough to cause the observed narrowing of the proton resonance.

For γ CD_3NH_3Cl, a broadening of the spectrum already begins at about 240 K, and at about 160 K the line shape is typical of a rigid equilateral proton triangle. This indicates a considerably slower reorientation rate for the NH_3 group compared to the CH_3 group. This is again in agreement with the T_1 data. Furthermore, an estimate of the activation energy was made giving good agreement with the value obtained from T_1 measurements (*cf.* Table 1).

Table 1. Summary of activation energies in kcal/mol obtained from NMR data for reorientations in CH_3NH_3Cl, CD_3NH_3Cl, and CH_3ND_3Cl. The data for the CH_3 group and NH_3 group reorientations are from CH_3ND_3Cl and CD_3NH_3Cl, respectively, except for the first value given for NH_3 in the γ phase. This value was obtained from CH_3NH_3Cl.

Method	Methyl group			Ammonium group			Reference
	α	β	γ	α	β	γ	
Second moment	–	4.4 (3)	–	–	5.1 (3)	7.3 (2) 6.9 (4)	Present data
T_1	0.81 (2)	5.0 (1)	2.5 (2)	0.93 (1)	6.5 (5)	7.7 (6)	1
Line width	–	4.8	–	–	6.1	–	8

This and other activation energies presented in this paper were calculated on the basis of the assumptions that (a) the correlation time τ for the reorientation has a temperature dependence given by

$$\tau = \tau_0 \exp{(E/RT)}$$

and (b) the relation between the second moment and τ is the one given by Gutowsky and Pake.[11]

The conclusions for the selectively deuterated samples are supported by the observations made on the non-deuterated specimen. On cooling, the spectrum broadens from that of rotating proton triangles to a superposition of such a spectrum on the spectrum of a rigid three spin system. The spectrum remains this way down to the lowest temperatures studied. A crude estimate of the second moment for CH_3NH_3Cl with a rigid NH_3 group gives 24 G^2 using the same structural data as Tsau and Gilson.[8] This compares well with the

measured plateau value of 25 G^2. The observation of this plateau also makes it possible to make a further calculation of the activation energy for the NH_3 reorientation, resulting in the value 6.9 kcal/mol.

2. *β Phase.* The results obtained for the β phase of the three specimens are very similar to those reported by Tsau and Gilson.[8] The conclusion is that their line-width transitions and activation energies refer to the β phase. The activation energies from the present study agree well both with their results and with the T_1 study.[1] The plateau values of the second moments are in general somewhat higher in the present case than in Ref. 8, and are closer to the calculated values. The different reorientation behaviour of the β and γ phases is clearly seen in Fig. 4, where spectra of β and γ CH_3NH_3Cl at 150 K are given. The spectrum from the β phase is closely similar to that of a rigid proton triangle. This is due to the low reorientation rate ($\ll 10^5$ Hz) both for the CH_3 and the NH_3 groups at this temperature. For the γ phase the spectrum also contains a narrow component. This is most probably from the CH_3 groups which reorient much more rapidly in this phase due to the considerably smaller activation energy (2.5 kcal/mol as compared to an average of 4.7 kcal/mol in the β phase).

One unusual feature is seen both for CH_3NH_3Cl and CD_3NH_3Cl when heating past the β to γ transition (*cf.* Figs. 1 and 2). The spectrum broadens considerably and discontinuously, indicating a sudden *lowering* of the reorientation rate for the NH_3 group when going to the high temperature phase. The relaxation theory of Bloembergen, Purcell and Pound [12] predicts an inverse proportionality between T_1 and the reorientation rate at low temperatures. Thus the sudden lowering of the reorientation rate should give a discontinuous increase of T_1 for CD_3NH_3Cl when going from the β to the γ phase. In fact, this is precisely what was observed.[1] In the vicinity of the phase transition at 220 K the relaxation time T_1 for CD_3NH_3Cl was 0.6 s and 35 s, respectively, for the β and γ phases. This implies a decrease in the reorientation rate by almost two orders of magnitude when heating past the transition. Clearly, this behaviour is at least qualitatively consistent with the observed difference in activation energies for the NH_3 group in the two phases.

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